Perfluoro- and Polyfluoro-sulphonic Acids. Part 22.[1] Polyfluorophenyl Pentafluorobenzenesulphonates and their Electron Transfer Reaction with Sodium Iodide

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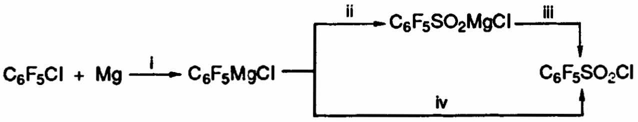
Polyfluorophenyl pentafluorobenzenesulphonates (**1**) have been synthesized in excellent yields by the reaction of pentafluorobenzenesulphonyl chloride with polyfluorophenoxides. Nucleophilic attack on **1** resulted in the breakage of the S–O bond accompanied by displacement of *o*- and /or *p*-fluorine. Reaction of **1** with sodium iodide (**8**) in a mole ratio of 1 :3 (**1**:**8**) yielded polyfluorodiphenyl ethers **9** and **10** as the main products. However, *p*-$C_6F_5OC_6F_4SO_3C_6F_5$ (**12**) was isolated as the major product in addition to **9** and **10** when the reactant ratio was 1 :1 or 1 :0.25. Reaction of **12** with sodium iodide also gave **9** and **10** when the reactant ratio was 1 :3 (**12** : **8**). The reaction of **1** (or **12**) with NaI is supposed to be an electron-transfer process.

Perfluoroalkanesulphonate esters have become useful and widespread reagents in both preparative and mechanistic organic chemistry.[2] Alkyl, vinyl, aryl,[2] perfluoroalkyl[3] and polyfluoroaryl[4] perfluoroalkanesulphonates have been synthesized in a variety of ways. Despite this, the preparation of polyfluorophenyl pentafluorobenzenesulphonates, $C_6F_5SO_3$-C_6F_4X-*p* (X = F, Cl, I) has not been reported in the literature even though there are, seemingly, no difficulties from a synthetic point of view. We were prompted to synthesize such compounds from the following observations.[4] Catalytic amounts of KF in diglyme are able to induce quantitative decomposition of perfluoroalkyl perfluoroalkanesulphonates $R_FSO_3CF_2R_F$ at −50 °C to give the corresponding sulphonyl and acyl fluorides. KCl reacted similarly but at 100 °C and KBr reacted only partially at 160 °C. However, KI reacted anomalously, *i.e.*, it readily induced complete decomposition of the ester at room temperature, the same products being formed accompanied by a small amount of iodine. The finding that addition of *p*-dinitrobenzene (a single-electron scavenger) to the reaction system inhibits the formation of iodine but no other products led us to suggest that iodide ion reacts with the ester *via* both an ordinary S_N2 on sulphur and a single electron transfer (SET) pathway.[3a] It was considered interesting to investigate the behaviour of other perfluorosulphonic esters *e.g.*, polyfluoroaryl perfluorobenzenesulphonate. Furthermore, to our knowledge, there is no other known SET process involving sulphonic esters and triflates.[5] Herein, we report the synthesis and reactions of polyfluorophenyl pentafluorobenzenesulphonate with several nucleophiles, in particular with sodium iodide.

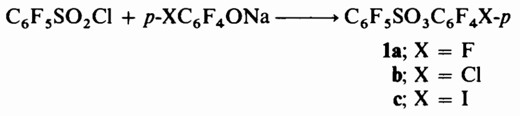
Results and Discussion

First, we modified the synthesis of pentafluorobenzenesulphonyl chloride by two methods, *i.e.*, treatment of pentafluorophenyl magnesium chloride in tetrahydrofuran (THF) at low temperature with sulphur dioxide followed by chlorine gas or directly with SO_2Cl_2 in one step (Scheme 1). The yield of sulphonyl chloride achieved was 50–60% as compared with 35% as given in the literature.[6,7]

Treatment of the sulphonyl chloride with sodium polyfluorophenoxide *p*-XC_6F_4ONa in diethyl ether at 0 °C for 0.5 h formed the corresponding sulphonate ester **1** in excellent yield (Scheme 2).



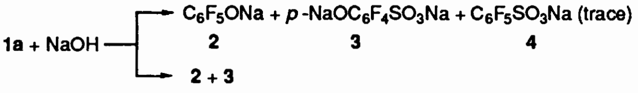
Scheme 1 *Reagents and conditions:* i, THF, −10 to −20 °C; ii, SO_2, −78 °C; iii, 0 to −5 °C; iv, SO_2Cl_2–hexane



$$C_6F_5SO_2Cl + p\text{-}XC_6F_4ONa \longrightarrow C_6F_5SO_3C_6F_4X\text{-}p \quad \begin{array}{l} \textbf{1a}; X = F \\ \textbf{b}; X = Cl \\ \textbf{c}; X = I \end{array}$$

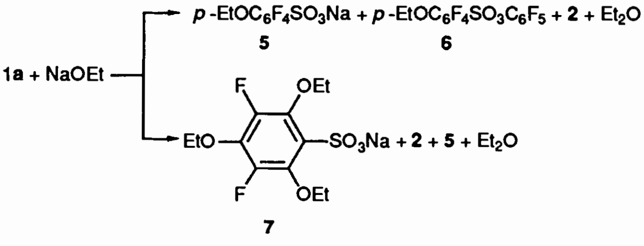
Scheme 2

Complete alkaline hydrolysis of **1a** occurred only in the presence of excess sodium hydroxide (**1a**:NaOH = 1:3) at 100 °C for 10 h giving the pentafluorophenoxide **2** and the disodium salt **3** (Scheme 3).



Scheme 3

Nucleophilic attack of ethoxide on **1a** in the reactant ratio 1:1 afforded **2**, sodium *p*-ethoxytetrafluorobenzenesulphonate (**5**), pentafluorophenyl *p*-ethoxytetrafluorobenzenesulphonate (**6**) and diethyl ether while the trisubstituted fluorobenzenesulphonate **7** (Scheme 4) was obtained in addition to **2** and **5** when the ratio was decreased to 1:6.



Scheme 4

We next focused our attention on the reaction of **1** with iodide ion. It was found that **1a** did not react with sodium iodide

Table 1 Reaction of **1** and **12** with **8** at 80 °C[a]

Entry	Reactants (mole ratio)	Additive (mol)	Reaction time (*t*/h)	Products (%)[b] **9**	**10**	**12**
1	**1a**:**8** (1:3)	None	10	46.6	29.7	—
2	(1:3)	Bu$^t_2$NO (0.15)	11	47.5	15.8	—
3	(1:3)	O_2	10	10.3	31.2	—
4	(1:3)	DAE (2)	11	2.2	52.8	—
5	(1:3)	*p*-DNB (0.20)	10	48.3	17.6	—
6	(1:3)	*p*-HQ (0.20)	10	7.4	33.5	—
7	**1b**:**8** (1:3)	None	8.5	29.9	43.1	—
8	**1c**:**8** (1:3)	None	12	33.4	22.2	—
9	**12**:**8** (1:3)	None	12.5	13.9	23.6	—
10	**1a**:**8** (1:1)	None	11	17.7	13.2	36.0
11	(1:1)	Bu$^t_2$NO (0.10)	10	12.0	9.0	34.8
12	(1:1)	O_2	10	2.0	12.0	41.5
13	(1:1)	*p*-HQ (0.20)	12.5	2.4	14.7	73.8
14	(1:1)	*p*-DNB (0.20)	11	21.5	7.2	62.2
15	(1:0.25)	None	10	1.5	1.5	62.5

[a] The conversion was complete. [b] Isolated yield.

(**8**) in diglyme at room temperature even after 10 h, however, at 80 °C the reaction was complete within 8.5–12.5 h, giving **9**, **10**, **11** and **12** as shown in Scheme 5.

$$\underset{\mathbf{1}}{C_6F_5SO_3C_6F_4X\text{-}p} + \underset{\mathbf{8}}{NaI} \xrightarrow{\text{i}} \underset{\mathbf{9}}{p\text{-}IC_6F_4OC_6F_4X\text{-}p} + \underset{\mathbf{10}}{p\text{-}HC_6F_4OC_6F_4X\text{-}p}$$

$$+ \underset{\mathbf{11}}{p\text{-}XC_6F_4OH} + \underset{\mathbf{12}}{(p\text{-}C_6F_5OC_6F_4SO_3C_6F_5)} + SO_2$$

Scheme 5 *Reagents and conditions:* i, diglyme, 80 °C, 8.5–12.5 h

The relative amounts of the products were strongly dependent on the ratio of the reactants. Diphenyl ethers **9** and **10** were the main products with a trace of **11** when the ratio was 1:3 (**1**:**8**). Another compound, **12**, was isolated as the major product in addition to **9** and **10** when the reactant ratio was 1:1 or 1:0.25 (see Table 1). In all the reactions neither dipentafluorophenyl sulphone $C_6F_5SO_2C_6F_5$ (**13**) nor pentafluoro(iodo)benzene was detected (*vide infra*). Compounds **9** and **10** could not be separated completely by means of column chromatography on silica gel or alumina. However, a small amount of pure **9** can be obtained on recrystallization of a mixture of eluates from methanol. Reduction of a mixture of **9** and **10** with Zn–CH_3CN or Zn–EtOH–HCl gave the pure compound **10** (Scheme 6).

$$\mathbf{9a,b} + \mathbf{10a,b} \xrightarrow{\text{i}} \mathbf{10a,b}$$

$$\mathbf{9c} + \mathbf{10c} \xrightarrow{\text{ii}} \mathbf{10d}\ (X = H)$$

Scheme 6 *Reagents and conditions:* i, Zn–CH_3CN, 80 °C, 6 h; ii, Zn–EtOH–HCl, reflux, 4 h

Interestingly, the same products, **9a** and **10a**, could be obtained from the reaction of **12** instead of **1** with NaI [reactant ratio 1:3 (**12**:**8**)] under the similar conditions. It is noteworthy that no ether of higher molecular weight, *e.g.* p-$(C_6F_5O)C_6F_4(OC_6F_4X)$-$p$ (X = H, **14a**; X = I, **14b**) was formed as inferred from the results obtained for **1**. When the ratio was changed to 1:1, in addition to **9a** and **10a**, some unchanged **12** was recovered, but again no sulphonate of higher molecular weight, *e.g.* p-$(C_6F_5O)C_6F_4(OC_6F_4SO_3C_6F_5)$ (**15**) was formed (*vide infra*).

$$\underset{\mathbf{12}}{p\text{-}(C_6F_5O)C_6F_4SO_3C_6F_5} + \underset{\mathbf{8}}{NaI} \xrightarrow{\text{diglyme}} \mathbf{9a} + \mathbf{10a}$$

Addition of a single-electron scavenger, such as *p*-DNB or Bu$^t_2$NO or free radical inhibitors such as *p*-hydroquinone (*p*-HQ) or oxygen to the reaction mixture in which reactant ratio was 1:3 (**1**:**8**), caused a reduction in the yield of **9** and/or **10** to some extent (see Table 1). Among them oxygen,[8] hydroquinone and diallyl ether (DAE) (Entries 3, 6 and 4, respectively) suppressed the yield of **9** significantly. In the case of reaction with the reactant ratio 1:1 (**1**:**8**) the suppression was not apparent except in the case of oxygen and hydroquinone, however, the yield of **12** was increased dramatically when *p*-DNB and hydroquinone were used as inhibitors. We have attempted to trap the pentafluorophenyl radical with DAE (Entry 4),[9] however, no expected tetrahydrofuran derivative was detected* although the relative yields of **9a** and **10a** changed significantly.

All these results in addition to the known ability of iodide ion to act as an electron donor[10] seem to indicate the possibility of an electron transfer mechanism shown in eqns. (1)–(8).

$$\underset{\mathbf{1}}{C_6F_5SO_3C_6F_5} + \underset{\mathbf{8}}{I^-} \longrightarrow \underset{\mathbf{1}^{\bullet -}}{[C_6F_5SO_3C_6F_5]^{\bullet -}} + I^\bullet \qquad (1)$$

$$\underset{\mathbf{1}^{\bullet -}}{[C_6F_5SO_3C_6F_5]^{\bullet -}} \longrightarrow \underset{\mathbf{16}}{C_6F_5SO_2^\bullet} + \underset{\mathbf{17}}{C_6F_5O^-} \qquad (2)$$

$$C_6F_5SO_2^\bullet \longrightarrow \underset{\mathbf{18}}{C_6F_5^\bullet} + SO_2 \qquad (3)$$

$$C_6F_5^\bullet + I^- \longrightarrow [C_6F_5I]^{\bullet -} \xrightarrow{\mathbf{1}} C_6F_5I + \mathbf{1}^{\bullet -} \qquad (4)$$

$$C_6F_5^\bullet + \text{‘H’} \longrightarrow C_6F_5H \qquad (5)$$

$$C_6F_5I + \mathbf{17} \longrightarrow \mathbf{9} \qquad (6)$$

$$C_6F_5H + \mathbf{17} \longrightarrow \mathbf{10} \qquad (7)$$

$$\mathbf{1} + \mathbf{17} \longrightarrow \mathbf{12} \qquad (8)$$

The initiation step is a one-electron transfer process from the iodide ion to the sulphonate **1** with the formation of the radical

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* $C_6F_5^\bullet$ generated from the photolysis of $C_6F_5SO_2Br$ can be trapped by DAE to give tetrahydrofuran derivatives $C_6F_5SO_2CH_2CHCH_2OCH_2CHCH_2Br$ (*cis*:*trans* = 3:1) and $C_6F_5SO_2CH_2CHCH_2OCH_2CHCH_3$ (*cis*:*trans* = 3:1).

anion ($1^{\bullet-}$) which decomposes to give the pentafluorobenzenesulphonyl radical **16** and pentafluorophenoxide **17**. The pentafluorobenzenesulphonyl radical **16** is assumed to be a very unstable species which instantaneously fragments to afford the pentafluorophenyl radical **18**. Radical **18** either reacts with iodide to give pentafluoro(iodo)benzene or abstracts hydrogen from the solvent to give pentafluorobenzene. Nucleophilic attack of **17** on pentafluoro(iodo)benzene and pentafluorobenzene resulted in the formation of **9** and **10**, respectively. In the presence of a higher concentration of iodide ion (*e.g.* **1**:**8** = 1:3), the decomposition of **1** goes to completion, **9** and **10** thus becoming the sole products. Whereas in the presence of a mole equivalent or catalytic amounts of sodium iodide or of some inhibitors, radical **16** and consequently radical **18** were produced in a limited amount, most of the pentafluorophenoxide **17** produced underwent the nucleophilic substitution on **1** to yield **12** [eqn. (8)].

The formation of **10** from the direct nucleophilic attack of **17** on pentafluorobenzene has been reported in the literature.[11] That of **9** from **17** and pentafluoro(iodo)benzene was clarified in a control experiment.

That **9a** and **10a**, as mentioned above, were the products from the reaction of both **12** and **1** can be readily explained by Scheme 7.

$$\underset{\mathbf{12}}{p\text{-}(C_6F_5O)C_6F_4SO_3C_6F_5} + I^- \longrightarrow \mathbf{12}^{\bullet-} + I^\bullet$$

$$\mathbf{12}^{\bullet-} \longrightarrow \underset{\mathbf{19}}{p\text{-}(C_6F_5O)C_6F_4SO_2^\bullet} + \underset{\mathbf{17}}{C_6F_5O^-}$$

$$\underset{\mathbf{19}}{p\text{-}(C_6F_5O)C_6F_4SO_2^\bullet} \longrightarrow \underset{\mathbf{20}}{p\text{-}(C_6F_5O)C_6F_4^\bullet} + SO_2$$

$$\mathbf{20} + \text{`H'} \longrightarrow \mathbf{10a}$$

$$\mathbf{20} + I^- \longrightarrow \mathbf{9a}^{\bullet-}$$

$$\mathbf{9a}^{\bullet-} + \mathbf{12} \longrightarrow \mathbf{9a} + \mathbf{12}^{\bullet-}$$

$$\mathbf{9a} + C_6F_5O^- \not\longrightarrow \underset{\mathbf{14b}}{p\text{-}(C_6F_5O)C_6F_4(OC_6F_4I\text{-}p)}$$

$$\mathbf{10a} + C_6F_5O^- \not\longrightarrow \underset{\mathbf{14a}}{p\text{-}(C_6F_5O)C_6F_4(OC_6F_4H\text{-}p)}$$

$$\mathbf{12} + C_6F_5O^- \not\longrightarrow \underset{\mathbf{15}}{p\text{-}(C_6F_5O)C_6F_4(OC_6F_4SO_3C_6F_5)}$$

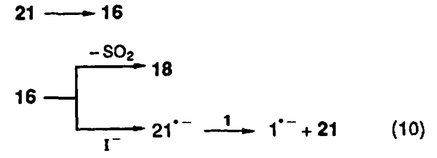
Scheme 7

Compounds **9a** and **10a** are apparently obtained from the reactions of radical **20**, generated from the decomposition of **19**, with iodide or 'hydrogen'. Pentafluorophenoxide is unable to attack on **9a** and **10a** to give **14b** and **14a**, respectively, because their *para*-positions are occupied by an electron donating rather than electron accepting group. This also applies to the absence of **15**.

The initiation step can be accounted for by a mechanism other than SET, namely that pentafluorobenzenesulphonyl iodide (**21**) may be an intermediate (*cf.* the recent discovery of the existence and 'pure' radical properties of analogous R_FSO_2I[12]). This intermediate may be formed from the attack of iodide on the sulphur of **1**. The iodide **21** would then

$$\underset{\mathbf{1}}{C_6F_5SO_3C_6F_5} + I^- \longrightarrow \underset{\mathbf{21}}{C_6F_5SO_2I} + C_6F_5O^- \quad (9)$$

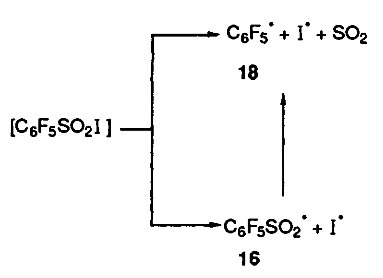
decompose to give **16** which either affords **18** after elimination of SO_2 or captures iodide ion to form radical anion $\mathbf{21}^{\bullet-}$ in the presence of excess of I^-. Pentafluorobenzenesulphonyl iodide (**21**) may be regenerated from $\mathbf{21}^{\bullet-}$ and **1** by an electron-transfer process (Scheme 8).



Scheme 8

In order to determine the role played by the intermediate **21** in the reaction, we attempted to synthesize this unknown compound. Treatment of a THF or ether solution of pentafluorobenzenesulphonylmagnesium chloride with 1 mol equiv. of iodine at 40 °C for 3 h gave no desired sulphonyl iodide but bis(pentafluorophenyl) sulphone (**13**) and pentafluoro(iodo)benzene in a ratio of 1:5. Use of CH_2Cl_2 as the solvent led to a product ratio of 1:2. Attempts to detect or trap the radicals **18** and **16** met with failure. The products obtained may result from the very fast radical decomposition of sulphonyl iodide which is even more unstable than its analogous R_FSO_2I.[12]

$$C_6F_5SO_2MgCl + I_2 \longrightarrow [C_6F_5SO_2I]$$



Scheme 9

We believe that pentafluorobenzenesulphonyl iodide, generated by SET and/or S_N2 on sulphur in the initiation step followed by SET [eqns. (10) and (9)], plays an important role especially in the reaction of **1** and **12** with a higher concentration of iodide. The absence of $C_6F_5SO_2C_6F_5$ and C_6F_5I in the reaction of **1** with **8** may be ascribed to the fast consumption of $C_6F_5^\bullet$ and easy nucleophilic substitution of C_6F_5I by $C_6F_5O^-$ (**17**).

Experimental

All boiling points and melting points are uncorrected. IR spectra were run on a Shimadzu IR-440 spectrophotometer. NMR spectra (chemical shifts in ppm from external Me_4Si for ^1H and from external CF_3CO_2H for ^{19}F NMR, positive for upfield shifts) were recorded on an EM-360 NMR spectrometer at 60 MHz. Mass spectra were taken on an MS-4201 instrument.

All solvents were dried and purified prior to use. All reactions were carried out under an atmosphere of pure nitrogen unless specified otherwise.

Preparation of $C_6F_5SO_2Cl$.—(*a*) Dried SO_2 was introduced slowly into a solution of C_6F_5MgCl (0.1 mol) in tetrahydrofuran (THF)[13] with stirring at −78 °C until the brown colour of the Grignard solution had disappeared (*ca.* 2 h) and ^{19}F NMR spectroscopy showed that $C_6F_5SO_2MgCl$ had formed. The mixture was allowed to warm to −5 °C over 1 h. Dried Cl_2 gas was bubbled slowly into the stirred solution at −5 to 0 °C, which caused the solution to become light yellow. When the conversion of $C_6F_5SO_2MgCl$ was complete (^{19}F NMR monitoring), the addition of Cl_2 gas was discontinued and the reaction mixture was stirred at room temperature for a further 2 h, then poured into cold water and extracted three

Table 2 ^{19}F NMR chemical shift of the fluorine *ortho* to the substituent (solvent: THF)

Compound	δ_F
C_6F_5Cl	64.3
C_6F_5MgCl	36.2
$C_6F_5SO_2MgCl$	70.3
$C_6F_5SO_2Cl$	59.8

times with CH_2Cl_2. The combined extracts were washed with saturated aq. Na_2SO_3, saturated aq. $NaHCO_3$ and water, and then dried over $MgSO_4$. Distillation gave 13–16 g of $C_6F_5SO_2Cl$ (50–60%), b.p. 86–88 °C/5 mmHg (lit.,[7] b.p. 75–76.5 °C/2 mmHg); $\delta_F(CCl_4)$ 56.8 (2 F, m), 63.2 (1 F, m) and 79.9 (2 F, m).

Although the reaction is 'one-pot', each step may be identified by ^{19}F NMR spectroscopy because of the large difference in chemical shift of the fluorine *ortho* to the substituent being changed in these compounds as shown in Table 2.

(*b*) In a 250 cm^3 three-necked flask, fitted with a magnetic stirrer, nitrogen inlet, a pressure-equalizing funnel and condenser with a dry tube, were placed SO_2Cl_2 (13.5 g, 0.1 mol) and dried hexane (50 cm^3). C_6F_5MgCl (prepared from 0.05 mol of C_6F_5Cl) in THF was added dropwise at 0 °C. The mixture was allowed to stir at room temperature for 2–3 h. Treatment of the reaction mixture as above gave $C_6F_5SO_2Cl$ (6.9 g, 52%), b.p. 72–74 °C/2 mmHg.

Synthesis of **1** *and* **12**.—*General procedure*. In a 100 cm^3 three-necked flask, fitted with a magnetic stirrer, nitrogen inlet and a pressure-equalizing funnel, were placed $C_6F_5SO_2Cl$ (7 g, 26.3 mmol) and dried THF (15 cm^3). Sodium pentafluorophenolate in Et_2O [prepared from C_6F_5OH (27.2 mmol) and Na (30.4 mmol)] was added dropwise at 0 °C in 0.5 h. The reaction mixture was stirred for a further 2 h at ambient temperature and then poured into water, extracted with Et_2O three times, washed with water and dried over $MgSO_4$. The solvent was removed and the product was chromatographed on silica gel, to give **1a** (9.8 g, 23.7 mmol, 90.1%), m.p. 38–40 °C (Found: C, 35.05; F, 45.75; S, 7.7. Calc. for $C_{12}F_{10}O_3S$: C, 34.80; F, 45.87; S, 7.74%); ν_{max}(pellet)/cm^{-1} 1640m, 1500s, 1420s, 1310m, 1200m, 1100m, 980s and 600s; $\delta_F(CH_3COCH_3)$ 57.0 (2 F, m), 64.5 (1 F, m), 76.3 (2 F, d, J = 18.6 Hz), 78.0 (1 F, t, J = 18.6 Hz), 81.5 (2 F, m) and 84.5 (2 F, t, J = 11.3 Hz); m/z (rel. intensity) 414 (8.2%, M^+), 231 (78.9, $C_6F_5SO_2^+$), 183 (42.3), 167 (40.4, $C_6F_5^+$), 155 (34.5), 117 (26.5) and 105 (100).

1b: m.p. 39.5–40.5 °C, yield 86.7% (Found: C, 32.85; Cl, 8.15; F, 40.5; S, 7.35. Calc. for $C_{12}ClF_9O_3S$: C, 33.47; Cl, 8.23; F, 39.70; S, 7.44%); ν_{max}(film)/cm^{-1} 1650m, 1500s, 1420s, 1200m, 1110m, 1080m, 1000s and 890m; $\delta_F(CH_3COCH_3)$ 59.2 (2 F, m), 65.0 (2 F, d, J = 18.6 Hz), 66.5 (1 F, m), 76.0 (2 F, d, J = 16.9 Hz) and 83.7 (2 F, m); m/z (rel. intensity) 432 (3.85%, M + 2), 430 (10.33, M^+), 231 (100, $C_6F_5SO_2^+$), 199 (29.92), 183 (26.21), 167 (71.38, $C_6F_5^+$) and 117 (43.20).

1c: m.p. 48–49.5 °C, yield 91.4% (Found: C, 27.35; S, 6.4. Calc. for $C_{12}F_9IO_3S$: C, 27.62; S, 6.14%; ν_{max}(film)/cm^{-1} 1650m, 1500s, 1420m, 1320m, 1200m, 1110m, 1000m, 980m and 820m; $\delta_F(CCl_4)$ 40.2 (2 F, m), 55.3 (2 F, m), 64.0 (1 F, m), 72.4 (2 F, d, J = 16.8 Hz) and 80.2 (2 F, m); m/z (rel. intensity) 522 (42.96%, M^+), 291 (86.17), 263 (60.68), 231 (100, $C_6F_5SO_2^+$), 215 (22.47), 167 (45.93) and 117 (73.95).

$C_6F_5SO_2Cl$ (45 mmol) in Et_2O was added dropwise to a solution of C_6F_5ONa (60 mmol) in Et_2O with stirring, at ambient temperature. The reaction mixture was allowed to stir for 0.5 h at 40 °C and then worked-up as usual. A mixture of **1a** and **12** (19.5 g) was obtained. ^{19}F NMR spectroscopy showed **1a**:**12** = 2.6:1. Yield: **1a**, 68.1%; **12**, 26.2%. After chromatography on silica gel, a small amount of pure **12** was obtained, m.p. 86.5–87.5 °C (Found: C, 36.8; F, 46.15; S, 5.65. Calc. for $C_{18}F_{14}O_4S$: C, 37.39; F, 46.00; S, 5.55%); ν_{max}(pellet)/cm^{-1} 1640w, 1530s, 1500s, 1425m, 1200m, 1160m, 1100m, 1000s, 765m and 620m; $\delta_F(CH_3COCH_3)$ 58.8 (2 F, t, J = 16.5 Hz), 76.6 (2 F, d, J = 16.9 Hz), 78.1 (2 F, d, J = 16.9 Hz), 79.4 (1 F, t, J = 22.6 Hz), 80.4 (2 F, d, J = 17.0 Hz), 83.5 (1 F, t, J = 19.7 Hz), 85.8 (2 F, t, J = 15.8 Hz) and 87.0 (2 F, t, J = 16.4 Hz). MS: m/z (rel. intensity) 395 (100, $M^+ - C_6F_5O$), 347 (27.12), 331 (66.99), 303 (33.01), 183 (63.00), 155 (49.21), 148 (22.04) and 117 (23.77).

Reaction of **1a** *with* NaOH.—**1a** (414 mg, 1 mmol), NaOH (40 mg, 1 mmol) and distilled water (5 cm^3) were placed in a Pyrex tube fitted with a screw cap. The mixture was stirred at 100 °C for 10 h and then extracted three times with Et_2O. The organic extract was washed with water and dried ($MgSO_4$). 265 mg of **1a** (as determined by TLC and ^{19}F NMR spectroscopy) were recovered. The extent of conversion of **1a** was 36%. The aqueous layer was concentrated under reduced pressure and ^{19}F NMR spectroscopy showed the crude residue to contain **2**, **3** and a trace of **4**. The residue was acidified with aq. HCl and extracted with Et_2O. The dried ($MgSO_4$) extract afforded C_6F_5OH (64.5 mg, 0.356 mmol, 98.8%). The aqueous acid was neutralized with aq. NaOH, and the water was removed under vacuum to give a white solid. Recrystallization of the solid from 95% ethanol gave **3** (40 mg, 38.3%). Compound **3** is highly hygroscopic, m.p. >250 °C, ν_{max}(pellet)/cm^{-1} 1630m, 1490s, 1280m, 1200s, 1160s, 1059m, 960s and 660s; $\delta_F(H_2O)$ 71.0 (2 F, m) and 90.0 (2 F, m); m/z (FAB) 313 ($M^+ + Na^+$) and 291 ($M^+ + 1$).

1a (414 mg, 1 mmol), NaOH (120 mg, 3 mmol) and distilled water (5 cm^3) were stirred at 100 °C for 10 h, after which time conversion was complete. Treatment of the mixture as above gave C_6F_5OH (146 mg, 79.3%) and **3** (100 mg); $\delta_F(H_2O)$ 71.3 (2 F, m) and 90.0 (2 F, m).

Reaction of **1a** *with* EtONa.—In a Pyrex tube were placed **1a** (414 mg, 1 mmol), EtONa (68 mg, 1 mmol) and absolute ethanol (4 cm^3). The mixture was allowed to stir at 80 °C for 10 h. The solvent was then removed under reduced pressure and a white solid was obtained. The solid was dissolved in water and extracted with Et_2O and the extract was washed with water and dried ($MgSO_4$). After chromatography on silica gel, **1a** (66 mg, 16.0%), **6** (70 mg, 19.0%) and C_6F_5OH (90 mg, 72.8%) were obtained.

6: m.p. 64–66 °C (Found: C, 38.1; H, 1.4; F, 38.4; S, 7.7. Calc. for $C_{14}H_5F_9O_4S$: C, 38.20; H, 1.14; F, 38.84; S, 7.28%); ν_{max}(pellet)/cm^{-1} 3000w, 1640m, 1520s, 1390m, 1200s, 1000s and 760m; $\delta_H(CCl_4)$ 0.85 (3 H, t, J = 7.0 Hz) and 3.80 (2 H, q, J = 7.0 Hz); $\delta_F(CCl_4)$ 58.7 (2 F, t, J = 16.9 Hz), 74.5 (2 F, t, J = 17.5 Hz); 78.4 (3 F, m) and 84.0 (2 F, q, J = 17.5 Hz); m/z (rel. intensity) 440 (1.58%, M^+), 257 (100, $M^+ - C_6F_5O$), 183 (28.73, $C_6F_5O^+$), 167 (17.00, $C_6F_5^+$), 137 (30.12), 117 (33.35) and 43.00 (18.32).

Treatment of the aqueous layer as above gave **5** (40 mg, 20.1%). It is highly hygroscopic, m.p. >250 °C; ν_{max}(pellet)/cm^{-1} 2900w, 1630m, 1460s, 1380w, 1210s, 1100s, 970s and 640s cm^{-1}; $\delta_F(H_2O)$ 65.0 (2 F, m) and 79.3 (2 F, m); m/z (FAB) 319 ($M^+ + Na^+$).

For the ratio **1a**:EtONa = 1:6, the reaction mixture was stirred at 80 °C for 10 h after which time the conversion was complete. Treatment of the reaction mixture as above gave C_6F_5OH (81.5%), **5** (50.1%) and **7** (61.9%). **7** is also highly hygroscopic, m.p. >250 °C; ν_{max}(pellet)/cm^{-1} 2940w, 1600m, 1470s, 1440s, 1380m, 1200s, 1020s, 870w and 640m; $\delta_F(H_2O)$ 71.0 (s); m/z (FAB) 371 ($M^+ + Na^+$).

In the reaction, Et_2O produced was detected qualitatively by gas chromatography.

Reaction of **1** *or* **12** *with* **8**.—*General procedure.* A mixture of **1a** (414 mg, 1 mmol), **8** (450 mg, 3 mmol) and diglyme (4 cm^3) was stirred at 80 °C in a Pyrex tube fitted with a screw cap. TLC and ^{19}F NMR spectroscopy showed the conversion to be complete after 10 h. The mixture was poured into cold water, extracted three times with Et_2O, and the extract was washed with water and dried ($MgSO_4$). The solvent was removed and the residue was chromatographed on silica gel, to give a mixture (314 mg) of **9a** and **10a**. ^{19}F NMR spectroscopy showed the ratio **9a**:**10a** to be 17:11, yield: **9a**, 46.6%; **10a**, 29.7%. Recrystallization of the mixture in methanol gave pure **9a**, m.p. 72–73 °C (Found: C, 30.95; F, 37.75; I, 27.6. Calc. for $C_{12}F_9IO$: C, 31.47; F, 37.33; I, 27.71%); ν_{max}(pellet)/cm^{-1} 1520s, 1490s, 1169w, 1080m, 1000m and 980m; $\delta_F(CCl_4)$ 41.8 (2 F, d, J = 17.5 Hz), 77.0 (2 F, d, J = 17.5 Hz), 78.7 (2 F, d, J = 19.2 Hz), 81.5 (1 F, t, J = 25.0 Hz) and 84.1 (2 F, t, J = 24.8 Hz); m/z (rel. intensity) 458 (100%, M^+), 303 (19.57), 291 (29.17), 263 (25.20), 183 (7.77), 117 (32.57) and 98 (10.15).

Reduction of **9** *to* **10**.—*General procedure.* The above mixture of **9a** and **10a** in acetonitrile was stirred with molar zinc powder at 80 °C for 8 h. Treatment of the reaction mixture as usual gave pure **10a**, m.p. 49.5 −50.5 °C (lit.,[11] 54–55 °C); $\delta_H(CCl_4)$ 7.02 (m); $\delta_F(CCl_4)$ 60.9 (2 F, m), 79.0 (4 F, m), 82.2 (1 F, t, J = 19.7 Hz) and 84.5 (2 F, t, J = 19.7 Hz); m/z (rel. intensity) 332 (100%, M^+), 313 (23.89, $M^+ - F$), 285 (21.70), 254 (27.33), 183 (36.81, $C_6F_5O^+$) and 167 (5.31).

9b: m.p. 101–102 °C (Found: C, 30.6; Cl, 7.45; F, 33.15; I, 26.7 Calc. for $C_{12}ClF_8IO$: 30.38; Cl, 7.47; F 32.03; I, 26.75%); ν_{max}(pellet)/cm^{-1} 1490s, 1130m, 980s, 885 and 810m; $\delta_F(CCl_4)$ 40.1 (2 F, d, J = 18.6 Hz), 62.0 (2 F, d, J = 18.6 Hz), 76.2 (2 F, d, J = 18.6 Hz) and 77.3 (2 F, d, J = 18.6 Hz); m/z (rel. intensity) 475 (28.34%, M + 2), 473 (100, M^+), 350 (11.33), 348 (37.70), 201 (15.13), 199 (57.13), 171 (77.27) and 117 (89.48).

10b: m.p. 59.5–61.5 °C (Found: Cl, 9.75; F, 43.05. Calc. for $C_{12}HClF_8O$: Cl, 10.17; F, 43.60%); ν_{max}(pellet)/cm^{-1} 1539s, 1500s, 1180w, 1125m, 1040w, 990w, 950m, 880w and 840w; $\delta_H(CCl_4)$ 6.90 (m); $\delta_F(CCl_4)$ 61.3 (2 F, m), 62.2 (2 F, d, J = 18.6 Hz), 78.1 (2 F, d, J = 18.6 Hz) and 79.0 (2 F, m); m/z (rel. intensity) 350 (35.27%, M + 2), 348 (100, M^+), 313 (27.21), 199 (30.08), 171 (37.79), 137 (25.04) and 99 (28.74).

9c: m.p. 126–127 °C (Found: C, 25.2; F, 27.0. Calc. for $C_{12}F_8I_2O$: C, 25.46; F, 26.85%); ν_{max}(pellet)/cm^{-1} 1480s, 1200s, 970s and 810m; $\delta_F(CCl_4)$ 42.2 (4 F, d, J = 19.0 Hz) and 77.0 (4 F, d, J = 19.0 Hz); m/z (rel. intensity) 566 (100%, M^+), 439 (22.04), 291 (84.22), 263 (75.23), 148 (79.86), 136 (34.63), 117 (48.13) and 98 (29.59).

10c: $\delta_F(CCl_4)$ 42.3 (2 F, d, J = 19.3 Hz), 61.8 (2 F, m), 79.5 (2 F, m) and 82.7 (2 F, m).

10d: m.p. 40–41 °C (Found: C, 45.4; H, 0.3; F, 47.4. Calc. for $C_{12}H_2F_8O$: C, 45.88; H, 0.64; F, 48.38%); ν_{max}(film)/cm^{-1} 2850w, 2700w, 1630w, 1520s, 1490m, 1100m, 1080m and 1000m; $\delta_H(CCl_4)$ 6.95 (m); $\delta_F(CCl_4)$ 61.2 (4 F, m) and 79.0 (4 F, m); m/z (rel. intensity) 314 (100%, M^+), 295 (25.52), 267 (23.53), 137 (62.62), 117 (13.10) and 99 (57.46).

Suppression Experiment.—*General procedure.* A mixture of **1a** (414 mg, 1 mmol), **8** (450 mg, 3 mmol), *p*-DNB (34 mg, 0.2 mmol) and diglyme (4 cm^3) were stirred at 80 °C in a Pyrex tube fitted with a screw cap. ^{19}F NMR spectroscopy showed the conversion to be complete after 10 h. Treatment of the reaction solution as usual gave the mixture (280 mg) of **9a** and **10a**. ^{19}F NMR spectroscopy showed the ratio **9a**:**10a** to be 11:4, yield: **9a**, 48.3%; **10a**, 17.6%.

The procedure involving the other inhibitors is similar to that above. The results are listed in Table 1.

Reaction of Sodium Pentafluorophenoxide with Iodopentafluorobenzene or Pentafluorobenzene.—*General procedure.* In a 25 cm^3 three-necked flask, fitted with a magnetic stirrer, nitrogen inlet, a pressure-equalizing funnel and reflux condenser were placed C_6F_5I (1.5 g, 5 mmol) and diglyme (5 cm^3). Sodium pentafluorophenoxide (5 mmol) in diglyme (5 cm^3) was added dropwise at ambient temperature. The mixture was stirred at 100 °C for 17 h and treated as usual. ^{19}F NMR spectroscopy and GC analysis showed that **9a** had formed (5.5%).

Under similar reaction conditions, **10a** (4.5%) was obtained from the reaction of C_6F_5H with C_6F_5ONa.

Reaction of $C_6F_5SO_2MgCl$ *with* I_2.—A solution of I_2 (12.7 g, 50 mmol) in Et_2O (80 cm^3) was added dropwise to a THF solution of $C_6F_5SO_2MgCl$ (prepared from 50 mmol of C_6F_5Cl) with stirring at 0 °C. The mixture was kept overnight (15 h) at room temperature (^{19}F NMR spectroscopy showed the extent of conversion to be 12% and the ratio C_6F_5I:$C_6F_5SO_2C_6F_5$ to be 3:1) and then stirred at 40 °C for 3 h, after which time reaction was complete. Treatment as usual gave 8.0 g of a mixture of C_6F_5I and $C_6F_5SO_2C_6F_5$ (**13**) in a ratio of 5:1. Yield: C_6F_5I, 42.8%; **13**, 8.6%. They were identified by ^{19}F NMR spectroscopy and GC by comparison with authentic compounds.[14,15]

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